RESEARCH

CHEMICALS AND FERMENTABLE BIOMASS VIA HYDROTROPIC AGENT PRETREATMENT

RENEWABLE ENERGY BRANCH

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PREFACE

This report is concerned with the treatment of wood with a hydrotropic agent (surfactant) in the form of sodium xylene sulphonate. The objective of the work was to render biomass carbohydrate components accessible to cellulase enzymes thereby converting wood to a fermentable raw material for alcohol production.

ABSTRACT

Pretreating and subsequently heating poplarwood to 140°C with six parts of 33% w/w sodium xylene sulphonate hydrotropic salt for up to 16 hours generated pulps and liquors containing dissolved lignin. Pulps after treatment with cellulase enzyme gave almost 50% yields fermentable sugars expresed as glucose. Lignin held in cooking liquor could be recovered only with difficulty as colloidal precipitates by addition of water. An assessment of costs to produce fermentable biomass and lignin based chemicals concluded that the hydrotropic agent treatment process could not compete with the steam explosion system developed by Stake Technology Ltd.

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EXECUTIVE SUMMARY

Hydrotropic pulping involves the removal of lignin from lignocellulosic materials by use of surface active agents. The method is attractive because the gentle solvating action of a hydrotropic agent does not involve the severe acid or alkaline reactions of conventional pulping processes.

The literature published by R.H. McKee and later workers has been reviewed with the objective of producing a fermentable biomass from low cost poplar species.

The process has been carried out on a poplarwood hybrid, Populus deltoides D38 to generate a pulp whose accessibility to cellulase enzyme, Maxazyme CL2000 as judged by D-glucose production is ~ 50%. This is greater than the 35% noted for Paprican's Hurricane Pulp prepared by comminution of poplarwood and comparable to the 45% observed for Procell, a steam exploded poplarwood produced by Stake Technologies Ltd. However, when the yield of glucose which could be produced enzymatically is calculated more realistically on the basis of the wood feed and not upon the pulp product, the hydrotropic agent pretreatment process does not look so attractive.

The reactions were conducted in a 33.3% w/w sodium xylene sulphonate (SXS) solution at 140°C for varying lengths of time up to 16 hours. The recovery of lignin solids containing SXS has been partly demonstrated and a possible use for this material as a phenol substitute in glue manufacture discussed.

The hydrotropic pulping process has been shown to require the evaporation of large volumes of water for lignin recovery and liquor regeneration. The levels of capital investment required for reactors and vapour recompression evaporators make the process non-competitive with the steam explosion process of Stake Technology.

The project was curtailed before all tasks envisaged in the orignal proposal were completed since the economics are not competitive with the Stake Technology steam explosion process to produce fermentable biomass.

1. OBJECT OF THE RESEARCH

The objective of the research is to increase accessibility of wood to cellulase enzymes through pretreatment using hydrotropic pulping agents in order to produce fermentable biomass from unused waste biomass.

An additional objective is to recover lignin from the pretreatment and determine its utility as a fuel and as a phenol substitute for use in plastics.

2. BACKGROUND TO HYDROTROPIC PULPING

2.1 Process Background

Hydrotropic pulping is a process patented in Canada by R.H. McKee in 1942 (1). The process involves treatment of lignocellulosic materials with an aqueous solution of sodium xylene sulphonate (SXS) at elevated temperatures. The lignin is dissolved in a micellar solution which is separated from the wood chips after reaction. The pulp is washed free of chemical and the combined lignin-containing liquor and washings after concentration is re-used up to six times. The concentrated liquor is then diluted to 11% w/w SXS at which level the lignin separates from solution. The settled lignin may be reclaimed for heat or for use as a phenol substitute in adhesive manufacture.

The lignin removing action from wood is due to surface active properties of the sodium xylene sulphonate hydrotropic agent. At 33% w/w in water, SXS acts like a detergent providing a means to bring lignin into water (2). The literature indicates that a certain amount of lignin hydrolysis may be required before the solvating action becomes effective. It also indicates that hydrotropic agent concentration is critical to maintain solvent action of the liquor. Dilution of SXS in the liquor to 11% w/w is sufficient to precipitate the lignin from solution. The literature has suggested a wash with

fresh hydrotropic liquor, after the cook has been drained, should preceed a water wash. This sequential washing of the chips can minimise redeposition of lignin onto cellulose.

Hydrotropic delignification is felt to occur in three stages (2):

1. Dissolution of the lignin in wood as a result of:

   - Acid catalysed cleavage of lignin-carbohydrate bond.

   - Hydrolysis of hemicelluloses.

2. Solubilization of cleaved lignin.

3. Solution reaction of dissolved carbohydrates and lignin.

The cooking process produces acids which further catalyse cellulose dissolution as well as lignin solubilization.

At a critical point in the cooking cycle the rate of cellulose degradation equals the lignin solubilization. Beyond that point lignin content of the pulp actually increases with more cooking time.

A number of salts have been investigated as hydrotropic agents (2). The salts investigated include:

- cymene sulphonates
- toluene sulphonates
- o-, m-, p-xylene sulpnonates
- benzene sulphonate
- naphthalene sulphonates

Both ammonium and calcium salts have proven to be less effective than sodium salts of the above sulphonic acids (2). In practice, sodium xylene sulphonate (SXS) has been found to have the following advantages over other hydrotropic agents:

1. SXS has strong solvent action in solutions as weak as 23% w/w.

2. SXS must be diluted to only one third of its working concentration (i.e. to 11% w/w) to precipitate dissolved lignin. This results in lower evaporation costs than other hydrotropic agents when recovery of cooking chemicals is considered.

3. SXS is readily available at low cost.

Russian work (2) has shown the utility of buffering the hydrotropic solution. The use of 6% w/w caustic soda in the SXS solution reduces build-up of organic acids during cooking. The decreased acidity results in pulps having increased mechanical strength which require shorter cooking times to equivalent delignification levels. Shortened cooking cycles could result in increased enzymatically accessible cellulose levels in pulps due to decreased hemicellulose hydrolysis (2).

2.2 Chemicals from Process Liquors

Dissolved hemicellulose carbohydrates including xylans are degraded during the cooking cycle. Domburg and Gromov (3) claim that solutions of "pure" SXS do not degrade solutions of pure xylose or xylan much faster than does hot water. They also note that sodium sulphate impurity in commercial SXS results in much more rapid degradation than pure SXS. Any commercial hydrotropic pulping process could therefore be expected to degrade dissolved hemicelluloses.

The extent of degradation reactions will result in low sugar levels in spent hydrotropic liquors. McKee did not find significant amounts of reducing sugars in product liquors, but did observe organic acids and furfural. Gromov and Odintsov (3) however, claim to have identified sugars in spent hydrotropic liquors.

The literature claims sugar in liquors may be utilized in two ways. First, sugar remaining in the dilute wash after lignin precipitation may be concentrated and used for fermentation. A second utilization allows sugars to degrade during subsequent cooking cycles to give useable end products including:

- Carbon dioxide
- Acetic acidic
- Formic acid
- Furfural

These chemicals may be recovered by condensing gas phase components in the digester head space (3). The concentration of furfural in the condensate approached 1.8% after a few cooking cycles representing a yield of furfural of 1.5% on oven dry wood. Other volatile organic acids could be recovered in a similar fashion. Experiments using solutions of xylan and xylose (3) demonstrated potential furfural production as high as 10% w/w based on xylan and 21% w/w based on xylose using a sodium sulphate contaminated liquor. Acetic acid production approached 10% w/w. It appears that much of the cellulose that dissolved reacted to form recoverable products. There was perceived to be difficulty in recovering soluble sugars if acid and furfural producing reactions were sufficiently fast in a commercial liquor (2).

2.3 Lignin Recovery

Hydrotropic cooking liquor may be re-used after cooking until the liquor is nearly saturated. For hardwood species this may be six or seven uses (4). The liquor may also become saturated with "trace impurities" after as many as thirty cooks (4).

The trace impurities include silica, iron and organic acids from furfural decomposition (4). The lignin is precipitated by dilution of the hydrotropic liquor to a low concentration. For 33% w/w sodium xylene sulphonate, dilution with two volumes of water per volume of

cooking solution separates the lignin as a precipitate. McKee claims to filter off the lignin and further process diluted liquor. The trace contaminants can be separated by addition of lime at 1/2% w/w of the dilute liquor. Precipitated contaminants are also separated by filtration and the purified liquor is concentrated by evaporation.

2.4 Use of Recovered Lignin

Poplar wood contains 24% lignin (5) and this component has value as fuel and potential as a phenol substitute for plastics and resin manufacture (2). The lignin in the wet precipitate may be concentrated by evaporation of the water to leave a residue suitable for use as a fuel.

The literature also indicates that hydrotropic lignin may be used as a low cost phenol substitute in the manufacture of plywood and particle board glues (2). Its use in this application is similar to substitution of lignin sulphonic acids from sulphite pulping of wood for phenol. Thus, Coyle describes glue made from sulphonated lignin isolated from sulphite mill waste liquor (6). Lignin sulphonate is pre-reacted with formaldehyde in caustic at an elevated temperture. The resulting product is then reacted with phenolic resin to give a reactive glue. A typical formulation dilutes dry sulphonated lignin to 40% w/w solids. Which is then added to an "advanced" phenol formaldehyde resin in concentrations from 25 to 50 % w/w based on solids.

A 50% lignin content glue produced chipboard having similar strength properties to a more expensive product containing 100% phenol formaldehyde adhesive.

A further development of such glue systems has been patented by Grunewald et al (7, 8). This process isolates only high molecular weight lignins for use in resin manufacture. Molecular weights over 1000 are claimed to produce superior resins. This patent proposes to

concentrate lignins by ultra filtration. The lignins may also include chlorinated lignin isolated from caustic extraction stage bleach plant effluent. The resins are claimed effective extenders for both phenol formaldehyde and for melamine formaldehyde glues.

Both glue systems referred to above claim cost savings of 30% over unextended conventional glues for equivalent strengths.

3. APPARATUS, MATERIALS AND METHODS

3.1 Reaction Vessels and Heating Bath

Reactions were carried out using four 325 mL stainless steel reaction vessels. The vessels were of heavy wall construction and were closed by screw-on gas tight lids sealed by thick silicon rubber O-rings.

The reaction temperature was maintained within 1°C by a Tenney Engineering Inc. batn insulated with 2 inches of styrofoam. The heat transfer fluid was glycerine. The bath was fitted with a motorized set of rollers which rotated the reaction vessels in the bath at 6.7 RPM. The whole apparatus was operated in a fume hood.

3.2 Wood

Wood used in these experiments was the same as used in the IEA Biomass Liquefaction Test Facility Project (5). The species was a poplar hybrid clone, Populus deltoides D38 harvested at 7 years, then debarked chipped, and dried slowly at room temperature to 10% moisture content. Trees were 12 meters high and 12.3 cm diameter at breast height. The wood analysis is shown in Table 1.

Table 1. Wood Feedstock Analysis

COMPONENT	% BY WEIGHT	METHOD
Extractives	3.0	Tappi std. T12 OS-75
Lignin	24.2	Acid insoluble Tappi std OS-74
Pentosan (Hemicellulose)	20.5	Tappi std. T223 OS-71
Cellulose	55.3	by difference
Ash	0.5	

Chipped wood was well mixed inside a large polyethylene drum and allowed to equilibrate for a few days before use. It was then weighed into small sealable plastic bags in 40 gram amounts and stored inside a refrigerator. Wood contained 9.75% w/w contained water.

3.3 Hydrotropic Agent Preparation

Sodium xylene sulphonate was supplied by Hart Chemical Company, Guelph, Ontario. Technical and material safety data sheets for a solution of SXS are included as Appendix 2. A 33% w/w solution of SXS in tapwater was prepared by dissolving 1000g SXS powder in 2 L of hot water. The pale brown coloured cloudy solution required filtration to remove suspended initial impurities before use in experiments.

3.4 Analytical Methodology

3.4.1 Enzyme assay for cellulase accessibility

The procedure descibed is based upon that used by Jurasek at the Pulp & Paper Research Institute of Canada Paprican (9). The cellulose enzyme, Maxazyme, used in this procedure was also obtained from Paprican.

3.4.1.1 Preparation of sodium acetate buffer

Acetic acid solution (0.2 M) was prepared by diluting 11.55 mL glacial acetic acid to 1000 mL with distilled water. Sodium acetate solution (0.2 M) was prepared by dissolving 16.4 g sodium acetate in distilled water and diluting to 1000 mL. A 0.07 M sodium acetate buffer, pH 5.0, was prepared by adding 14.8 mL of acetic acid solution to 35.2 mL of sodium acetate solution and diluting to 100 mL with distilled water.

3.4.1.2 Preparation of cellulase enzyme solution

Frozen Maxazyme CL 2000, (500 mg), was weighed into a beaker, mixed with 100 mL acetate buffer and 5 mg thymol added to prevent microbial growth. The mixture was warmed to 30°C in a water bath and stirred for 10 minutes. The soluion was filtered through a glass fibre filter by vacuum filtration and the filtrate used for the enzymatic hydrolysis test.

3.4.1.3 Hydrolysis of pulps with cellulase enzyme

Desiccator dried and ground samples, (50 mg), were weighed into 50 mL Erlenmeyer flasks and incubated with 5 mL enzyme solution for 24 hours at 30°C. The flasks were shaken continuously.

At the end of the incubation period, hydrolyzates were centrifuged at 6500 gravity units for 15 minutes. The supernatants were then analyzed for reducing sugars as described in Section 4.4.1.4 below.

Samples of dried and ground pulp, (50 mg), were also carried through the same procedure, excluding the Maxazyme solution, but with the addition of 5 mL of 0.2 M sodium acetate buffer. This experiment gave the reducing sugars present in the sample before enzymatic hydrolysis. A sample of enzyme solution and buffer was also carried through the entire procedure to provide blanks for enzyme activity and

reagent absorbance. Hurricane pulp, a cominuted poplar, was included in tests over the period of the project as a control to determine whether enzyme activity was being maintained.

3.4.1.4 Analysis for reducing sugars produced by cellulase enzyme

Reducing sugars were determined in the hydrolysis supernatants colorimetrically following reaction with dinitrosalicylic acid (10).

Dinitrosalicylic acid reagent was prepared by dissolving 10.6 g of 3,5-dinitrosalicylic acid and 19.8 g sodium hydroxide in 1416 mL distilled water. To this solution were added 306 g sodium potassium tartrate, 7.6 mL of 90% phenol in water, and 8.3 g sodium metabisulfite.

One millilitre (1 mL) of hydrolysis supernatant was pipetted into a screw capped test tube followed by 1 mL of distilled water and 2 mL of dinitrosalicylic acid reagent. The test tube was sealed, the contents mixed, and the tube heated in a boiling water bath for 15 minutes.

The contents were diluted with 16 mL of distilled water and mixed well. Absorbances of the samples, glucose standards, enzyme-buffer and wood blanks were read at 575 nm using distilled water as a reference. The reducing substances present were estimated from a calibration curve of glucose concentration versus absorbance, and recorded as percent glucose.

Small corrections were applied to the percent glucose in incubated samples for absorbance due to enzyme-buffer and non-incubated pulp. (It should be noted that xylose and other non-glucose reducing sugars produced by enzymes were all recorded arbitrarily as percent glucose).

3.4.2 Estimation of reducing sugars in spent cooking liquors

The procedure described below is an adaptation of the Swedish Pulp & Paper Standard Method No CCA 11 & 12 for determination of fermentable sugar in sulphite waste liquor.

3.4.2.1 Reagents

Copper sulphate reagent (Fehling's Reagent) was prepared by dissolving 69.4 g of $CuSO_4 \cdot 5H_2O$ in water and diluting to 1 L. Alkaline sodium potassium tartrate solution was prepared by dissolving 350 g of this salt ($C_4H_4O_6KNa \cdot 4H_2O$) and 100 g of sodium hydroxide in water and diluting to 1 L. Analytical grade potassium iodide, 0.100 N sodium thiosulphate and thyodene indicator were used in the iodimetric titrations. 5N sulphuric acid was used for acidification purposes.

3.4.2.2 Procedure

Spent cooking liquors were analyzed for reducing sugars before and after acid hydrolysis of dissolved polysaccharides. Hydrolysis was performed by treating 5 mL of the spent cooking liquor with 10 mL of 1N sulphuric acid at 120°C for 2 hours. This was achieved by heating the mixture in a test tube retained in a pressure cooker operating at 15 psi above atmospheric pressure. The mixture was then diluted to 25 mL with water prior to estimation of their reducing sugar levels.

Ten millilitres (10 mL) each of the copper sulphate reagent and alkaline tartrate solutions were pipetted into a 250 mL Erlenmeyer flask together with 20 mL of water and some boiling chips. This mixture was then placed on a preheated electrical hot plate and boiled for exactly 3 minutes. After this time, 10 mL of the solution containing the reducing sugar to be estimated was added. After 1 minute the liquid was boiling again and boiling was continued for a further 2 minutes (total of 3 minutes elapsed from addition of sugar solution). The flask contents were then cooled rapidly to 20°C using a stream of cold water; 1 g of potassium iodide was then added, followed by 10 mL of 5N sulphuric acid. Finally, the liberated iodine was titrated using the 0.1N sodium thiosulphate ("a" mL). A blank using 10 mL of water in place of the sugar solution was determined ("b" mL) and the net consumption of thiosulphate calculated ("a" -

"b"). The amount of reducing sugar in the sample expressed as grams per litre (g/L) was then taken from the table attached to this report as Appendix 1.

3.4.3 Experimental procedure

Stainless steel reactors were each charged with 40 g (wet) of wood chips held in a packed configuration by stainless mesh screens. Sodium xylene sulphonate solution (250 mL 33% w/w) was added to cover the chips leaving 10% void volume in the reactors. After tops were screwed in place reactors were weighed. For a normal cook, the reactor was pretreated at 90°C for 1/2 hour. (The pretreatment allowed liquor to penetrate chips before the temperature was raised for the reaction). The reactor was then transferred to the 140°C glycerine bath and rolled continuously to allow liquor circulation. The chips themselves did not mix inside the reactor. After the reaction, the vessels were submerged in cold water to stop the cooking process. Cooled vessels were then dried, opened and re-weighed to determine any weight loss due to gas loss or leakage. Reactions were performed in sets of four to determine the degree of data scattering.

Following reaction, liquor was drained from the vessels and the chips washed twice in the reactor with 200 mL water. The wash was collected and then the chips were transferred to a Waring blender and disintegrated in 750 mL of water. The resulting pulp was filtered through a Buchner filter funnel and the filtrate returned through the pulp mat a second time to collect fine particles. The pulp was usually dried at 105°C. However, one series of experiments compared drying methods in order to determine its effect on enzyme accessibility.

4. RESULTS AND DISCUSSION

4.1 Solids Balance

There are two incoming and four exiting streams which contain solids in the bench scale hydrotropic pulping process:

- wood
- sodium xylene sulphonate solution
- spent liquor containing solids
- chip wash containing solids
- blender wash containing solids
- pulp product

Figure 1 illustrates the relationship of these streams to the process. Samples of each liquor stream were dried at 105°C to determine the solids contents. The results of the solids balance are given in Table 2.

The solids balance accounts for the majority of components in each cook. Solids recovery decreases as reaction time is increased (Figure 2) indicating that gaseous products increases with time. These products are believed from study of the literature to include furfural, acetic acid, carbon dioxide and other volatile organic acids.

The solid loss must be due to degradation of lignocellulose if one reasonably assumes no experimental nor thermal decomposition losses of hydrotropic agent. After 16 hours reaction time, ~7% of the solids or 7.69 g of the input is not recovered. Since the incoming wood charge is 36.1 g the loss due to formation of volatile organic products can represent 21% by weight of the wood. This loss is very close to the weight of hemicelluloses in the poplar wood feed (20.5%).

FIG.1 SOLIDS CONTAINING STREAMS IN HYDROTROPIC PULPING PROCESS

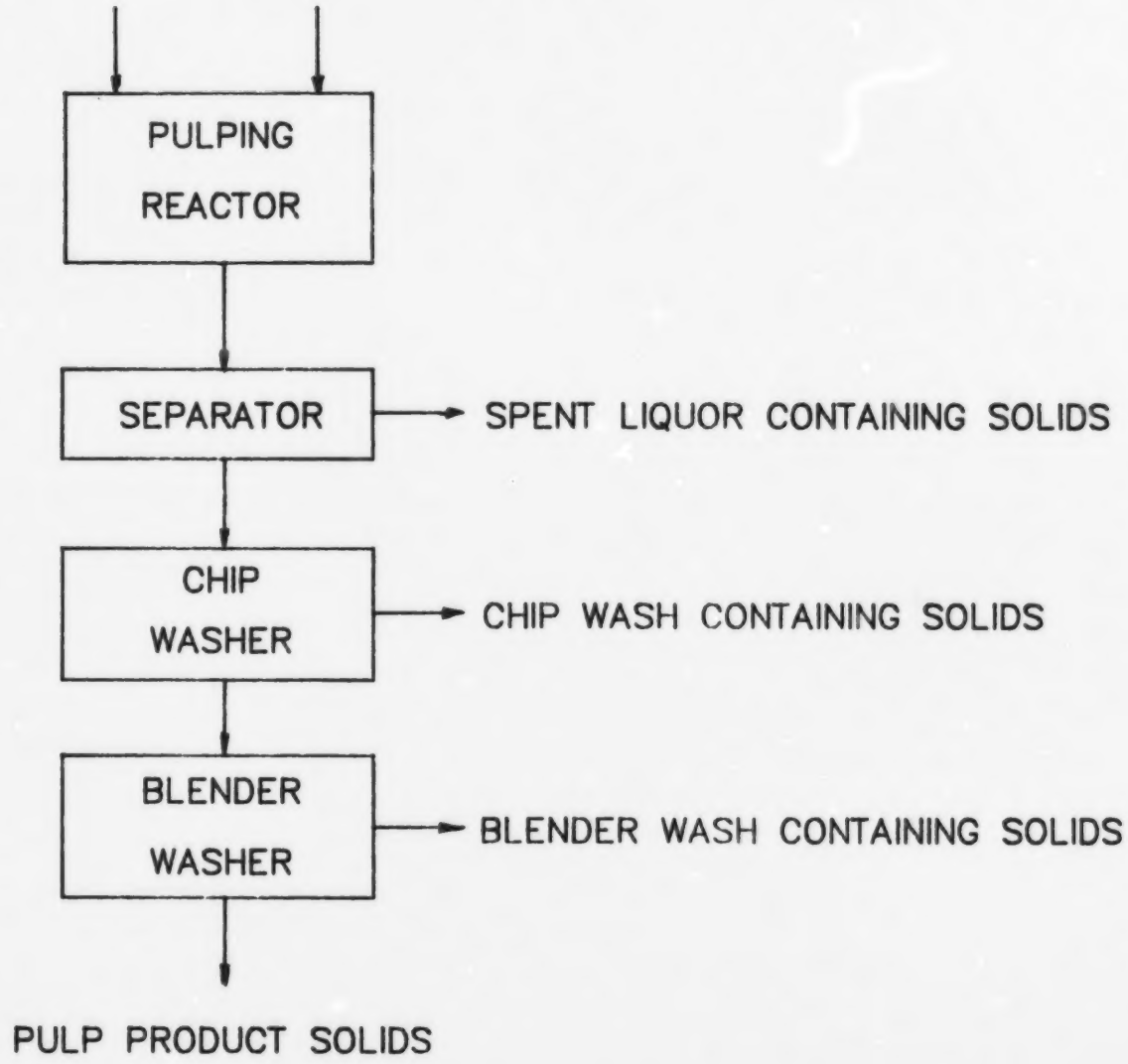
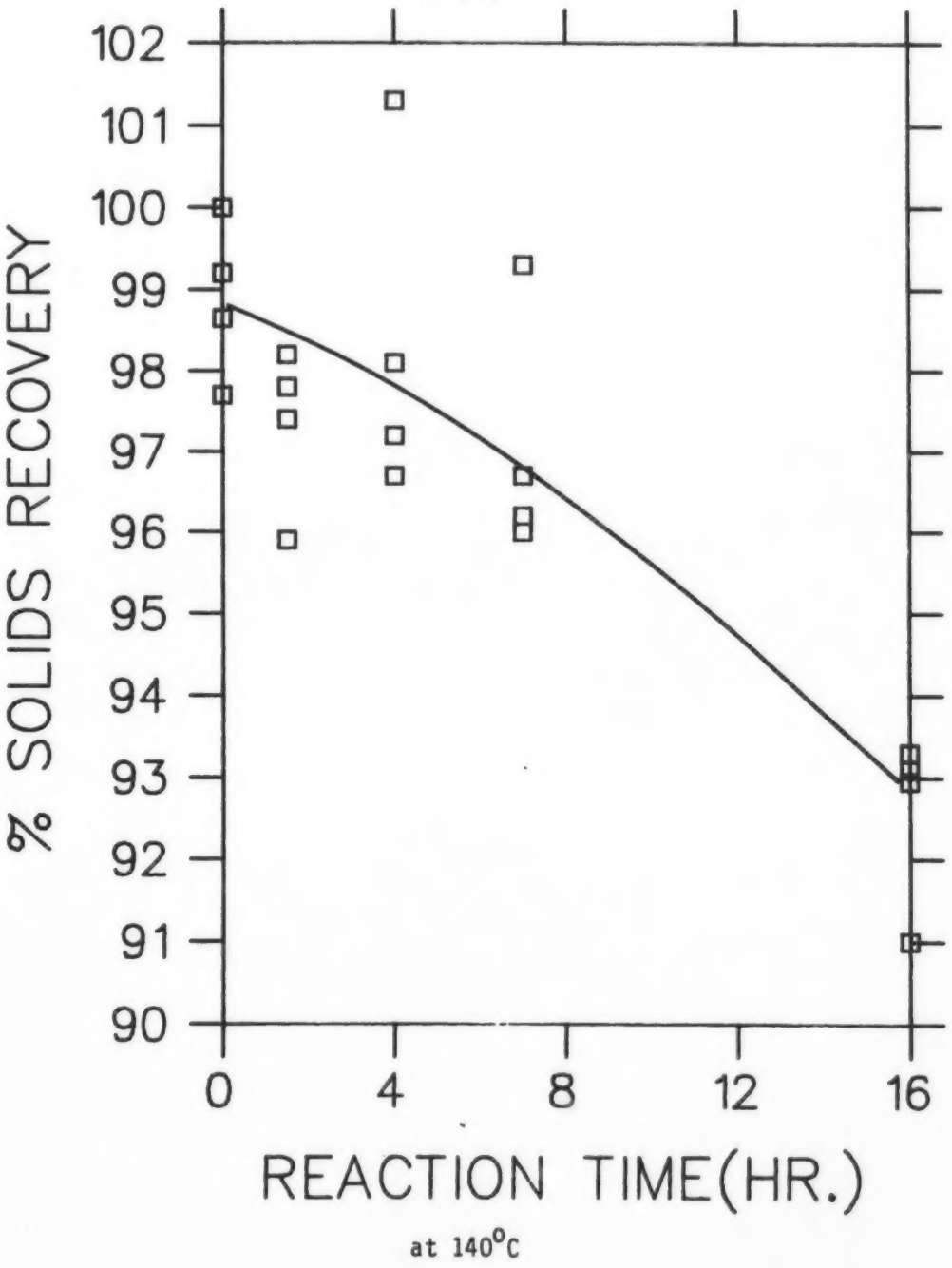


Table 2. Solids Balance

Run #	DRY WOOD IN (g)	SXS LIQUOR SOLID IN (g)	DRY PULP OUT (g)	LIQUOR & WASH SOLID *(g)	BLENDER SOLIDS (g)	GASEOUS WEIGHT LOSS (g)	REACTION TIME (hr)	SOLIDS RECOVERY % (wt)
1	36.1	73.8	23.1	66.72	10.24	0.5	16	91.0
2	36.1	73.8	22.7	68.87	10.96	0.4	16	93.3
3	36.1	73.8	23.2	68.03	11.10	0.4	16	93.1
4	36.1	73.8	22.5	67.83	11.84	0.5	16	93.0
5	36.1	73.8	33.8	64.53	9.62	-	1 1/2	98.2
6	36.1	73.8	32.9	61.88	10.64	-	1 1/2	95.9
7	36.1	73.8	32.4	66.96	7.74	-	1 1/2	97.4
8	36.1	73.8	33.0	68.01	6.51	-	1 1/2	97.8
9	36.1	73.8	24.2	74.84	6.53	0.2	7	96.1
10	36.1	73.8	24.2	74.94	6.42	0.3	7	96.0
11	36.1	73.8	24.4	78.38	6.31	0.7	7	99.3
12	36.1	73.8	23.4	76.34	6.58	0.2	7	96.7
13	36.1	73.8	26.4	74.71	10.60	-	4	101.6
14	36.1	73.8	26.3	72.24	8.33	-	4	97.2
15	36.1	73.8	26.0	72.5	7.82	-	4	96.7
16	36.1	73.8	26.1	74.4	7.31	-	4	98.1
17	36.1	73.8	36.3	69.55	5.10	-	1/2	100.0
18	36.1	73.8	37.7	66.48	4.14	-	1/2	98.6
19	36.1	73.8	36.0	66.02	5.40	-	1/2	97.7
20	36.1	73.8	36.5	67.14	5.44	-	1/2	99.2

* (SXS, lignin, sugars etc.)

FIG.2. SOLIDS RECOVERY AS A FUNCTION OF TIME at 140°C



In the 16 hour duration run (No. 1), a weight loss of only 0.5 g due to formation of products which are gaseous at room temperature was observed. The major loss was due to formation of water soluble materials which are volatilized at 105° during drying. Such substances would include acetic acid, furfural etc.

4.2 Pulp Yield

The yield of pulp from bone dry wood as a function of reaction time is shown in Figure 3. The pulp yield increases above 100% for the first period of the cooking cycle. This suggests the first part of the cook involves SXS penetrating chip walls to become associated with lignin. Subsequent to this period, hydrolysis reactions cleave lignin from cellulose (2) and cause it to dissolve in the liquor.

As the reaction proceeds, dissolved lignin passes through the cell wall and into the bulk of the cooking liquor. The majority of lignin is removed within 4 hours at 140°C. Further yield loss is due to removal of hemicellulose from the wood. After 16 hours, the observed yields of approximately 64% are consistent with total removal of hemicelluloses (supported by solid losses noted above) and removal of approximately 64% of the lignin in the poplar (24.2%). The brown colour of the pulp supports some residual lignin is left in the pulp.

4.3 Pulp Accessibility

The accessibility of both oven and air dried pulps to cellulase enzyme as a function of reaction time is represented graphically in Figure 4 from pulp and sugar yield data taken from Tables 2 and 3 respectively.. It is clear that cooking times in excess of 4.5 hours do not substantially increase sugar yields. A 37% yield of reducing sugars (expressed as glucose) is achieved at 4 1/2 hours. This yield is based on a pulp which was dried completely (bone dried). As will be discussed later, air drying may increase this yield to 45% w/w.

FIG.3 PULP YIELD AS A FUNCTION OF REACTION TIME at 140°C

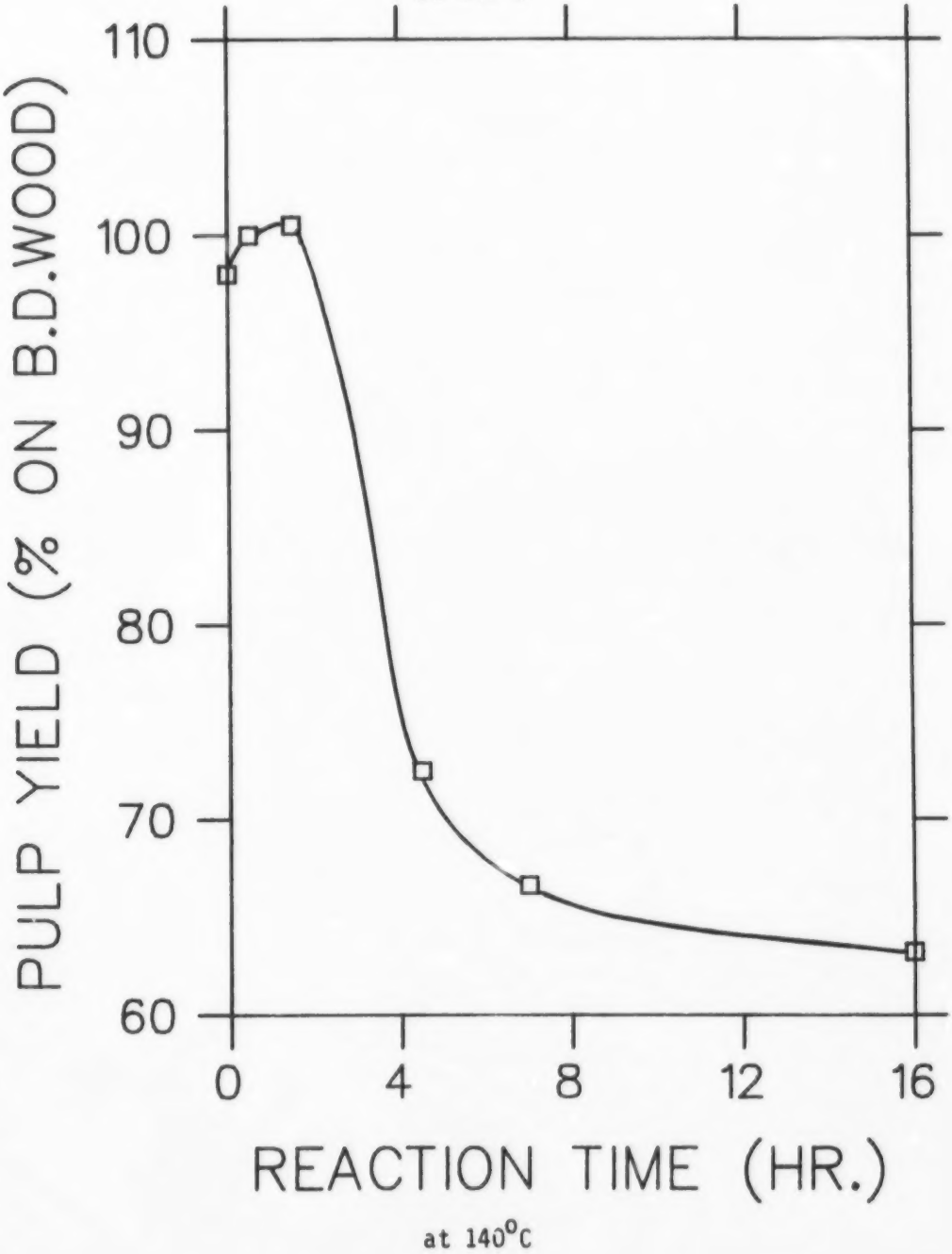


Table 3. Sugar Balance Including Hydrotropic Liquors

RUN NO.	RX. TIME (hr)	PRE HYD.[1] SUGAR (g/L)	POST HYD.[2] SUGAR (g/L)	LIQUID VOLUME (L)	SUGAR IN LIQ (g)	SUGAR IN PULP[3] (g)	SUGAR TOTAL[4] (g)	SUGAR % ON WOOD[4]
5-8	1.5	1.76	1.87	.517	.97	3.97	4.94	13.7
13-16	4.5	-	3.25	.504	1.64	9.20	10.84	30.0
9-12	7.5	-	3.00	.501	1.50	9.96	11.46	31.7
1-4	16.5	3.46	2.38	.464	1.10	9.74 (B.D.)	10.85	30.0
1-4	16.5	3.46	2.38	.464	1.10	11.73 (A.D.)*	12.83	35.5
Hurricane								35.0

*A.D. = air dry
B.D. = bone dry

1. Sugar prior to hydrolysis expressed as glucose.
2. Sugar after hydrolysis expressed as glucose.
3. Sugar in pulp from 36.1 g O.D. wood.
4. Assuming the sugar from the liquor could be recovered by some means and utilized.

The Hurricane pulp sample used as a control is a poplar wood prepared by a comminution process developed by the Pulp & Paper Research Institute of Canada. The accessibility of Hurricane pulp is 35%. However, the poplar wood used to prepare this sample was different from that used in our work so that direct comparison may not be valid.

The percentage sugar production based on wood feed as opposed to pulp product is shown in Figure 5. These values permit comparison of cominution with hydrotropic lignin removal. It will be seen that air dried samples of hydrotropic pulp have similar accessiblity to cellulase as Hurricane pulp (~32%). The oven dried samples were lower in accessibility to this enzyme. The final drying stages appear to change the material in a way which reduces enzyme accessibility.

The increase in accessibility due to air drying the pulp is seen in Figures 4 and 5.

Any future commercial process to produce fermentable cellulose would pass wet pulp to an enzymatic digester for sugar production. The accessibility of wet pulp could not be determined because neither this material nor frozen pulp could be ground for laboratory testing purposes. The more favourable data on air dried pulp is therefore the only applicable information for estimation of commercial yields.

Three poplar wood pretreatment processes under current investigation, viz comminution (Hurricane), hydrotropic pulping and the steam explosion process developed by Stake Technology Ltd. (Procell) produce materials having similar cellulase accessibilities based on wood input (15). The enzyme reactor producing sugar would be designed differently for the three substrates due to the varying lignin contents of the products to be fermented. Comminution and wood exploding processes retain the lignin in the product. This lignin will pass into the enzyme reactor and result in a heavy lignin sludge in this vessel in addition to undigested cellulose in the feed charge. This sludge will amount to 24% by weight of poplarwood if

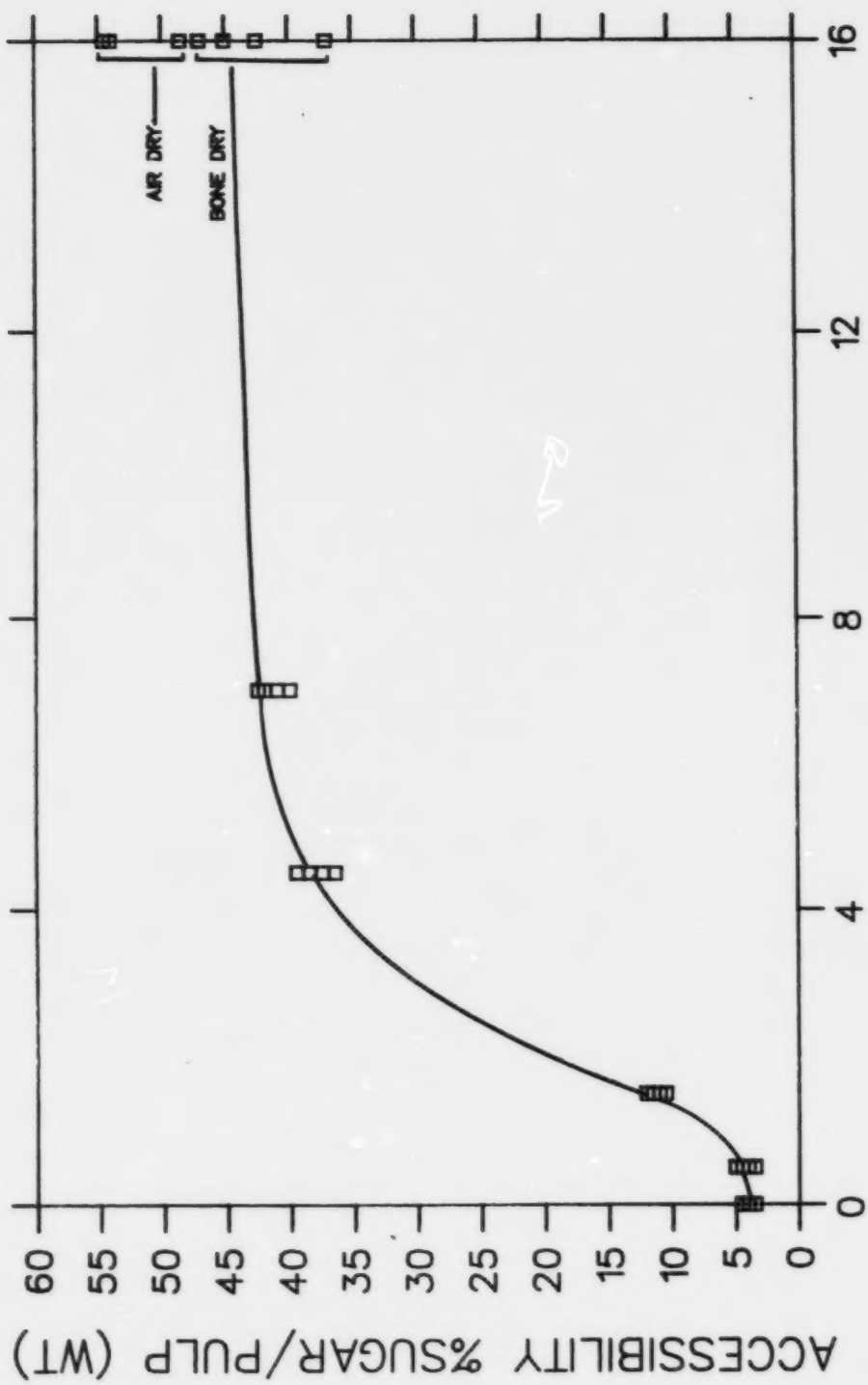
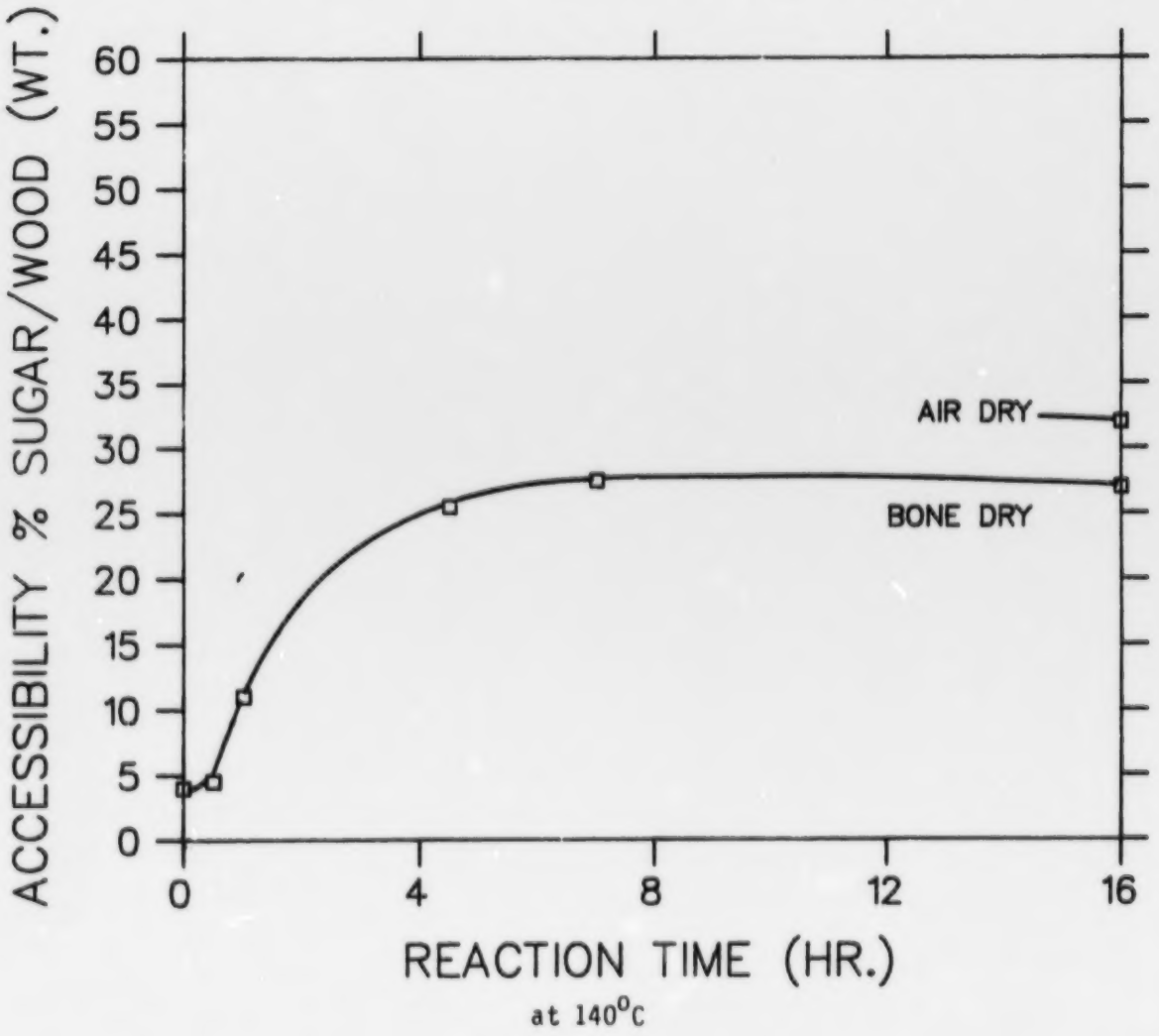


FIG.4
ACCESSIBILITY OF CELLULOSE (% ON PULP) VS. REACTION TIME AT 140°C

FIG.5

ACCESSIBILITY OF CELLULOSE (% ON WOOD) VS. REACTION TIME AT 140°C



this is the raw material undergoing fermentation. This is appreciable. It is therefore apparent that for given sugar production levels, the hydrotropic pulping process will require a smaller reactor to accomodate a smaller volume of sludge to be subsequently removed, dewatered and burned.

4.4 Lignin Recovery

Combined spent cooking liquors were diluted with two volumes of water which caused the liquor to become cloudy. Centrifugation at 1063 G did not result in a significant amount of sedimentation of the almost colloidal lignin precipitate. It is possible that liquors richer in lignin, such as those having contacted wood more than once, might have produced a lignin precipitate which would have readily sedimented in a manner similar to that described by McKee (1).

The combined, diluted spent liquors were allowed to stand for seven days and the lower one third volume containing the lignin-rich layer was isolated using a separatory funnel. This layer was found to contain 12.6% w/w solids.

After drying, the solids were found to contain 7.3% w/w sulphur. The SXS used in this study contained 15% sulphur indicating that the solids contain ~50% SXS. Clearly the inability of lignin to form an easily separated, compact precipitate means that such slurries will have to be exchanged with water several times in order to produce lignin with suphur contents low enough to be suitable for use as fuel.

Such lignin washing would not consume extra water if water destined for the saturated liquor lignin precipitation stage was employed.

Recovered "lignin" from the 12% w/w centrifugate was dried at 105°C. The solids were measured for higher heating value in an oxygen bomb calorimeter. The heat content was found to be 4789 cal/g (8621 BTU/lb) which includes a significant contribution from the S X S "impurity". A summary of the solids properties from drying the 12% w/w precipitate is shown in Table 4.

Table 4. Properties of Unwashed Lignin Precipitate

Solid content*	12.6% w/w
Sulphur*	7.3% w/w
Higher heat content of solids	4789 cal/g (8621 BTU/lb.)

* dry weight basis

4.5 WASTE LIQUOR SUGAR RECOVERY

Hydrotropic liquor and wash streams from each run were combined to determine total soluble sugar content using the Fehling's reagent procedure (3.4.2). Liquors were analysed before and after acid hydrolysis. Table 3 indicates the soluble sugar content of pulping liquors. The sugar content peaks at 4.4% based on wood in the 4.5 hour cook (runs 13-16). Further cooking decreases this sugar level, presumably due to either furfural or acid production. Efficient recovery of sugar in the cooking liquor will therefore prove difficult due to these reactions if liquor is re-used many times.

5. PROCESS FLOW SHEET ANALYSIS

5.1 The Liquor Flowsheet

A flowsheet is shown in Figure 6. The flowsheet is modeled around a path as seen by the liquor for a batch sequence of six reactions. The liquor path is chosen since one original batch of liquor will see six lots of wood before it is reconstituted to fresh liquor. This path differs from the flow of the wood alone.

In an operating plant, a single digester would be used and the liquor would be cycled six times. A continuous digester would be used and one sixth of the liquor flow would be continuously processed for lignin recovery.

FIGURE 6

PROCESS FLOWSHEET ANALYSIS

The liquor flowsheet was prepared using a VAX computer with the DECALC spreadsheet program. Each of the streams in and out of the reactor are defined by the content of the corresponding streams from our laboratory experiments. The solids balances and separation efficiencies are also as found in our experiments.

Assumptions in deriving this sheet include the following:

1. All lignin and SXS from pulp is recovered in washer 1 and recycled to the process.

2. All lignin recovery is done at the lignin separator.

3. SXS contained in lignin is recoverable by washing.

4. Solids balance and lignin recovery are taken from our laboratory experimental data.

5. Natural gas is available at B.C. prices for a small user.

6. Vapour recompression evaporation is used for weak liquor reconcentration and for pulp drying.

7. The basis of calculation is 1000 L of SXS liquid entering the first reactor.

As seen in Figure 6, each 1000 L liquor charge is cooked with 180.5 kg O.D. wood. At the conclusion of the cook the liquor is drained and the pulp is washed twice with 1000 L of water. Drained volumes are indicated on the flowsheet. Makeup liquor is added to drained liquor from reactor 1 and the second reaction is carried out for another 180.5 kg of poplar. A similar sequence is followed for six cooks using the same liquor with make-up.

Drained liquor following reaction 6 is diluted by wash liquor from the #1 and #2 washer lines. Some of wash #1 is evaporated to recycle as 33% SXS solution. The diluted liquor precipitates a lignin portion containing 12% solids which is washed with an equal volume of water. Wash water is assumed to remove all SXS and is then recycled to the first wash stage shown for reaction 6. This sequence recovers the SXS. The liquor leaving the lignin separator is evaporated to reform 33% SXS solution. The washed lignin is evaporated to dryness for sale as product.

Pulp is assumed to be oven dried to determine drier heat requirements, the heat source is assumed to be natural gas.

The products of one liquor cycle from six cooks are listed in Table 5. The sugar in the cooking cycle is assumed to be non-recoverable due to the difficulty in separating glucose from SXS in the diluted liquor stream. The dissolved sugars will eventually decompose to furfural and volatile organic acids. These compounds may be recovered for sale. Unrecovered solids and non-condensable gases account for nearly 16% of the wood charge.

Table 5. Products of One Liquor Cycle

Wood In	kg	1083
Pulp Out	kg	784.8
Lignin Out	kg	126
H_2O Evaporated	kg	10352.8
Wash Sewered	L	2317.7
H_2O Input	L	12666
Unrecovered and non-condensable	kg	172.2
% on O.D. wood		15.9

Some of this loss could be due to the fact that lignin recovery data are based on information from liquor used only once. It is possible that higher lignin recovery efficiencies would be obtained using a more saturated material.

5.2 Operational Cost Analysis

The cost of the hydrotropic process is dependent upon the efficiency of evaporation and upon the recovery of hydrotropic liquor. The evaporation cycle is chosen to be thermo compression (vapour recompression) due to its high efficiency. The pulp drying cost is also calculated based on vapour recompression evaporation costs. This is not a normal pulp drying method, but could be adapted for use where thermal energy is expensive, possibly in this process where lignin is sold instead of burned. The higher capital cost of this system is not included here. Yundt (11) claims a heat requirement of 20,000 Kcal per metric ton of water evaporated for thermo compression evaporation.

The efficiency of SXS recovery will greatly influence operational cost. The large volumes of wash water make evaporation of all the wash impractical, hence, the sewered wash will have some SXS content. This has been estimated at 5% of the total SXS charged in one liquor cycle. Proctor (2) quotes SXS losses for McKee's process would be between 1.7 and 3.4% on pulp. We assume roughly twice these estimated SXS losses.

The product values are calculated by assuming a yield of glucose of 50% on pulp (the air dry case). The value of glucose produced is estimated at one third that of refined sucrose (12). Thus product glucose value is U.S. $0.24 Kg (CDN. $0.34/kg) using the U.S. $0.726/kg (CDN $1.02/kg) price for sucrose quoted in the March 24, 1986 Chemical Marketing Reporter. The one third level is believed to provide an economic incentive to enzymatically convert the pulp to glucose instead of using sucrose.

The lignin value for adhesive manufacture depends upon several factors. Variables include reactivity of lignin relative to that of phenol and the product being manufactured with the glue (16). Lignins vary in reactivity depending on the type of pulping process, lignin extraction method and liquor processing as history. Most lignins are not as reactive as phenol, therefore a longer period of hot pressing

may be required to produce a plywood sheet having strengths equivalent to those manufactured using entirely phenol based glue. A longer hot press time will result in lower production rates and increased costs. Forintek estimate that plywood mills could use up to a 15% w/w substitution of lignin for phenol. The low substitution level reflects adhesive qualities may not be as uniform as required by plywood manufactures. Chip board manufacturers on the other hand, may substitute 50% w/w lignin for phenol in glue. The 15% and 50% substitutions of lignin for phenol in plywood and 50% for chipboard manufacture are suggested as maximums for maintaining normal production rates (16).

Clearly glue manufacturers cannot pay lignin prices that are close to those of phenol otherwise there would be no reason to use lignin. Phenol traded for U.S. $0.25/lb (CDN $0.77/kg) as quoted in the March 24, 1986 Chemical Marketing Reporter. A realistic price for lignin might therefore be half that of phenol (ie. CDN $0.385/kg).

The wood cost is estimated by Forintek (13) at CDN $25/$M^3$ assuming 100 km hauling distance. The density of poplar is estimated at 337 kg/m^3 dry (13).

Three cases have been compared to determine an operating cost estimate (Table 6). The three cases assume our postulated returns for glucose and lignin in case A, and lower levels of return for cases B and C. These costs do not include any allowance for capital costs to pay for the process equipment. Such costs would be significant, but difficult to estimate at this stage.

Table 6 indicates that for simple process operation costs, the process will <u>not</u> break even for any of the three cases studied. Capital costs would further increase the loss incurred by operating this process.

If the SXS losses were to be less than the 5% postulated, the economics of case A might allow a <u>slight</u> return on operating costs. The lost SXS is 55% of the operating total cost, thus it's recovery presents the greatest opportunity for cost saving in the process.

Table 6. Operating Costs Estimate

BASIS: One Liquor Cycle of 1000L Used Six Times with Make-up[1]

	Case A	Case B	Case C
Glucose 392.4 kg			
glucose price	CDN $ 0.34/kg[2]	$ 0.20/kg	$ 0.10/kg
glucose credit	133.42	78.48	39.24
Lignin 126 kg			
lignin price	CDN $ 0.38/kg[3]	$ 0.20/kg	$ 0.10/kg
lignin credit	48.51	25.20	12.60
TOTAL CREDITS	$181.93	$103.68	$ 51.84
COSTS			
WOOD 1083 kg	80.34[4]		
SXS LOSS 61 kg	105.6[5]		
N. Gas 0.866 GJ	3.85		
TOTAL COSTS	$189.84	$189.84	$189.84
RETURNS	$-7.91	$-86.16	$-138.00

1. Information taken from Fig. 6 in which 1000 L liquor was contacted with 1083 kg of poplar wood. Products were 784.8 kg dry pulp having a glucose content of 392.4 kg and a lignin product weighing 126 kg.
2. Glucose price set at one third that of sucrose.
3. Lignin price set at one half that of phenol.
4. Wood price CDN $0.074/kg.
5. SXS price CDN $1.73/kg.

6. COMPETITIVE POSITION

The purpose of the hydrotropic pulping process is to produce enzymatically degradable cellulose and to provide a source of lignin-based chemicals. This process requires 4 hours cooking at 140°C and considerable water evaporation.

A major competitive process is that developed by Stake Technologies Ltd. (14). This process treats wood chips at high temperatures and high steam pressures (240°C 5 MPa) for a short time interval (~2 min). The product pulp has similar accessibility to cellulase as hydrotropic pulp. The yield from steaming, in contrast to hydrotropic pulping, is 95% due to retention of most of the lignin and loss of about 5% w/w of the hemicellulose.

The capital costs of a hydrotropic facility requiring digesters, evaporators, associated chemical plant and a steam plant are believed greater than the costs of the steam plant and steam cannon needed to produce steam exploded wood pulp. The lack of operating returns seen in Table 6 strongly suggest that the hydrotropic process would probably not be competitive with the Stake steam explosion process. With capital costs included, the hydrotropic process most certainly would not be competitive or economic.

One favourable but minor point for hydrotropic agent pretreatment is that lignin would be removed from wood. This would be of advantage to the design of an enzymatic hydrolyser for ethanol production. The hydrolysis reactor would have less sludge to remove from the spent pulp charge. This would allow smaller vessels to be used having lower capital costs.

7. CONCLUSIONS

The hydrotropic pulping process generates a product which after treatment with cellulase gives nearly a 50% yield of glucose. The process will also allow the isolation of lignin from cooking liquor and lignin could be used in adhesives and other chemical manufacturing.

The process is not competitive with a steam explosion process developed by Stake Technology Ltd. due to plant costs, large volumes of water which must be evaporated and loss of sodium xylene sulphonate cooking chemical.

REFERENCES

1. McKee, R.H. Can. Pat. 407066 (Sept. 1, 1942).

2. Procter, A.R. Pulp Paper Mag. Can. 72 (8):67 (1971).

3. Domberg, G.E., Gromov, V.S. Khimicheskaya Pererabotka i Zashchita Drevesiny, Riga, Akad Nauch Latv. SSSR. 1964:53-60.

4. McKee, R.H. U.S. Patent 2,308,564 Jan., 1943.

5. Beckman, D. Biomass Liquefaction Test Facility Program. IEA Cooperative project D1 Final report, Vol. 3, p.4, 1983.

6. Coyle, R.P., Canadian Patent 992682, 1976.

7. Grunewald, K.H., Mansson, I.G. U.S. Patent 4,292,216, Sept. 1981.

8. Grunewald, K.H., Mansson, I.G. Canadian Patent 1150441, 1983.

9. Jurasek, L. 1979. Enzymatic hydrolysis of pretreated aspen wood. Developments in industrial microbiology. Vol. 20, p. 177.

10. Miller, G.L. 1959. Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugars. Analytical Chemistry 31, 426.

11. Yundt, B. Chemical Engineering, Dec. 24, 1984, p. 46.

12. Mueller, J.C. B.C. Research, Vancouver, B.C., private communication.

13. Middleton, G. Forintek, Vancouver, B.C., private communication.

14. Bender, R. Stake Technologies Ltd. U.S. Patent 4,136,207, Jan. 24, 1977.

15. Howard, J. Production of Livestock Feed from Unused Forest Biomass using Hydrotropic Agents. B.C. Research. Agriculture Canada contract No. OSB83-00622.

16. Steiner, P. Forintek, Vancouver, B.C., private communication.

APPENDIX 1

Relationship Between

Thiosulphate Titre and Glucose Weight

APPENDIX 1

Relationship Between Thiosulphate Titre & Glucose Weight (Fehling's Reagent Titration)

Tabellen und Tafeln (zu Kapitel IV).

Tabelle 77. *Bestimmung von reduzierendem Zucker in Kalilaugelösung nach der verfeinerten Methode von Schoorl.*

(Schoorl'sche Standard-Methode OCA II. - 1942).

0,1-n Thiosulfat ml	Glukose mg	0,1-n Thiosulfat ml	Glukose mg	0,1-n Thiosulfat ml	Glukose mg	0,1-n Thiosulfat ml	Glukose mg
1,0	3,1	6,4	20,4	11,8	38,4	17,2	57,1
1,2	3,7	6,6	21,1	12,0	39,1	17,4	57,8
1,4	4,4	6,8	21,7	12,2	39,7	17,6	58,5
1,6	5,0	7,0	22,4	12,4	40,4	17,8	59,2
1,8	5,6	7,2	23,0	12,6	41,1	18,0	59,9
2,0	6,3	7,4	23,7	12,8	41,8	18,2	60,6
2,2	6,9	7,6	24,3	13,0	42,5	18,4	61,3
2,4	7,6	7,8	25,0	13,2	43,2	18,6	62,0
2,6	8,2	8,0	25,6	13,4	43,9	18,8	62,7
2,8	8,8	8,2	26,3	13,6	44,6	19,0	63,4
3,0	9,5	8,4	26,9	13,8	45,3	19,2	64,1
3,2	10,1	8,6	27,6	14,0	45,9	19,4	64,8
3,4	10,8	8,8	28,2	14,2	46,6	19,6	65,5
3,6	11,4	9,0	29,0	14,4	47,3	19,8	66,2
3,8	12,1	9,2	29,7	14,6	48,0	20,0	67,0
4,0	12,7	9,4	30,3	14,8	48,7	20,2	67,7
4,2	13,4	9,6	31,0	15,0	49,4	20,4	68,5
4,4	14,0	9,8	31,7	15,2	50,1	20,6	69,3
4,6	14,6	10,0	32,3	15,4	50,8	20,8	70,0
4,8	15,3	10,2	33,0	15,6	51,5	21,0	70,8
5,0	15,9	10,4	33,7	15,8	52,2	21,2	71,5
5,2	16,6	10,6	34,4	16,0	52,9	21,4	72,3
5,4	17,2	10,8	35,1	16,2	53,6	21,6	73,1
5,6	17,8	11,0	35,7	16,4	54,3	21,8	73,9
5,8	18,5	11,2	36,4	16,6	55,0	22,0	74,7
6,0	19,2	11,4	37,1	16,8	55,7		
6,2	19,8	11,6	37,7	17,0	56,4		

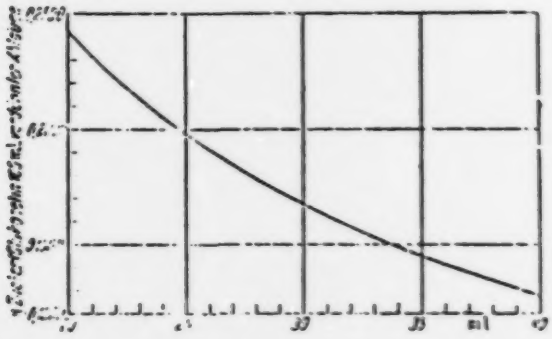


Abb. 135. Titration von Fehling'scher Lösung mit Sulfitablauge. Gerundete Abhängigkeit vom Verbrauch an Lauge (ml 0,1-n Thiosulfat-Lösung (Abszisse) und dem Zuckergehalt (Ordinate) gemäß der auf S. 315 beschriebenen Methode.

APPENDIX 2

Technical Data for

Sodium Xylene Sulphonate Hydrotropic Agent

HART CHEMICAL LIMITED
GUELPH CANADA

Technical Data

SXS POWDER

SXS POWDER is a hydrotrope for powdered built detergent systems to prevent instability and precipitation caused by electrolytes.

TYPICAL PHYSICAL PROPERTIES INCLUDE

Chemical Nature	-	Sodium Xylene Sulphonate
Physical Form	-	Powder
Colour	-	White
Active, Wt. %	-	90.0 Min.
Sulphate, Wt. %	-	7.0 Max.
Water, Wt. %	-	3.0 Max.
pH, 40% Aq. Sol'n.	-	7.5 - 10.5
Solubility, 40% Aq. Solution	-	Clear Soluble

STORAGE AND HANDLING

Storage in a dry area is recommended to avoid absorption of moisture. When wet or in solution, this material is corrosive to carbon steel and aluminum.

Normal safety equipment such as rubber gloves, eye protection and dust masks should be worn. In case of skin or eye contact, flush well with water. If irritation persists, seek medical aid.

THE RECOMMENDATIONS AND DATA PRESENTED ARE BELIEVED TO BE CORRECT HOWEVER NO WARRANTY IS EXPRESSED OR IMPLIED REGARDING THE ACCURACY OF THE DATA OR THE RESULTS OBTAINED FROM THE USE OF THIS INFORMATION, OR THAT ANY SUCH USE WILL NOT INFRINGE ANY PATENT

HART

256 VICTORIA ROAD SOUTH, GUELPH, ONTARIO, N1H 6K8
TELEPHONE (519) 824-3280 • (416) 270-8501

MATERIAL SAFETY DATA SHEET

SECTION I PRODUCT IDENTIFICATION

CHEMICAL NAME	Sodium Xylene Sulfonate	TRADE NAME	SXS-40
CHEMICAL FAMILY	Anionic Surfactant - Hydrotrope		

SECTION II HAZARDOUS INGREDIENTS

NAME	%	TLV (Units)	NAME	%	TLV (Units)

SECTION III PHYSICAL DATA

BOILING POINT (°C)	100	SPECIFIC GRAVITY (H_2O = 1)	1.190
MELTING POINT (°C)		PERCENT VOLATILE BY VOLUME (%)	57
VAPOR PRESSURE (kPa)	2.4	EVAPORATION RATE (Ether = 1)	< 1
VAPOR DENSITY (AIR = 1)	< 1	SOLUBILITY IN WATER	N/A
APPEARANCE AND ODOR	Clear yellow liquid, mild odor		

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) (°C)	93 (PMCC)	FLAMMABLE LIMITS	LEL N/A	UEL N/A
EXTINGUISHING MEDIA	Not applicable. Not flammable. Water solution			
SPECIAL FIRE FIGHTING PROCEDURES	Water may be used to cool containers			
UNUSUAL FIRE AND EXPLOSION HAZARDS	Pressure will develop in closed containers if they are heated above 100°C			

SECTION V HEALTH HAZARD DATA

EFFECTS OF OVEREXPOSURE	
SWALLOWING	May cause nausea and vomiting
SKIN ABSORPTION	None currently known
INHALATION	Mist may irritate nasal passages
SKIN CONTACT	Prolonged skin contact may cause irritation
EYE CONTACT	Painful and irritating

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HART CHEMICAL LIMITED
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pH, 40% Aq. Sol'n.	-	7.5 - 10.5
Solubility, 40% Aq. Solution	-	Clear Soluble

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SECTION VI EMERGENCY AND FIRST AID PROCEDURES

SWALLOWING	Give 2 glasses of water and induce vomiting by putting finger down throat. Call a physician
SKIN	Flush skin with water
INHALATION	If vapours are irritating remove to fresh air. If symptoms persist call a physician
EYES	Flush eyes thoroughly with plenty of water Call a physician

SECTION VII REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID	None
	STABLE	X		

INCOMPATABILITY *(Materials to avoid)* Materials that react with water

HAZARDOUS DECOMPOSITION PRODUCTS If burned, sulfur dioxide, carbon dioxide, carbon monoxide and smoke may be formed

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VIII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED Flush away with water or soak up with sand, or sweeping compound and shovel into waste containers

WASTE DISPOSAL METHOD Bury, incinerate or flush to sewage disposal system in accordance with all Federal, Provincial and Local Regulations

SECTION IX SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION *(Specify type)* None

VENTILATION	LOCAL EXHAUST	Normal room ventilation	SPECIAL
	MECHANICAL *(General)*		OTHER

PROTECTIVE GLOVES	Rubber	EYE PROTECTION	Goggles or face mask

OTHER PROTECTIVE EQUIPMENT Eye bath and safety shower

SECTION X SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid heating above 100°C

Store at 35°C minimum to prevent crystallization

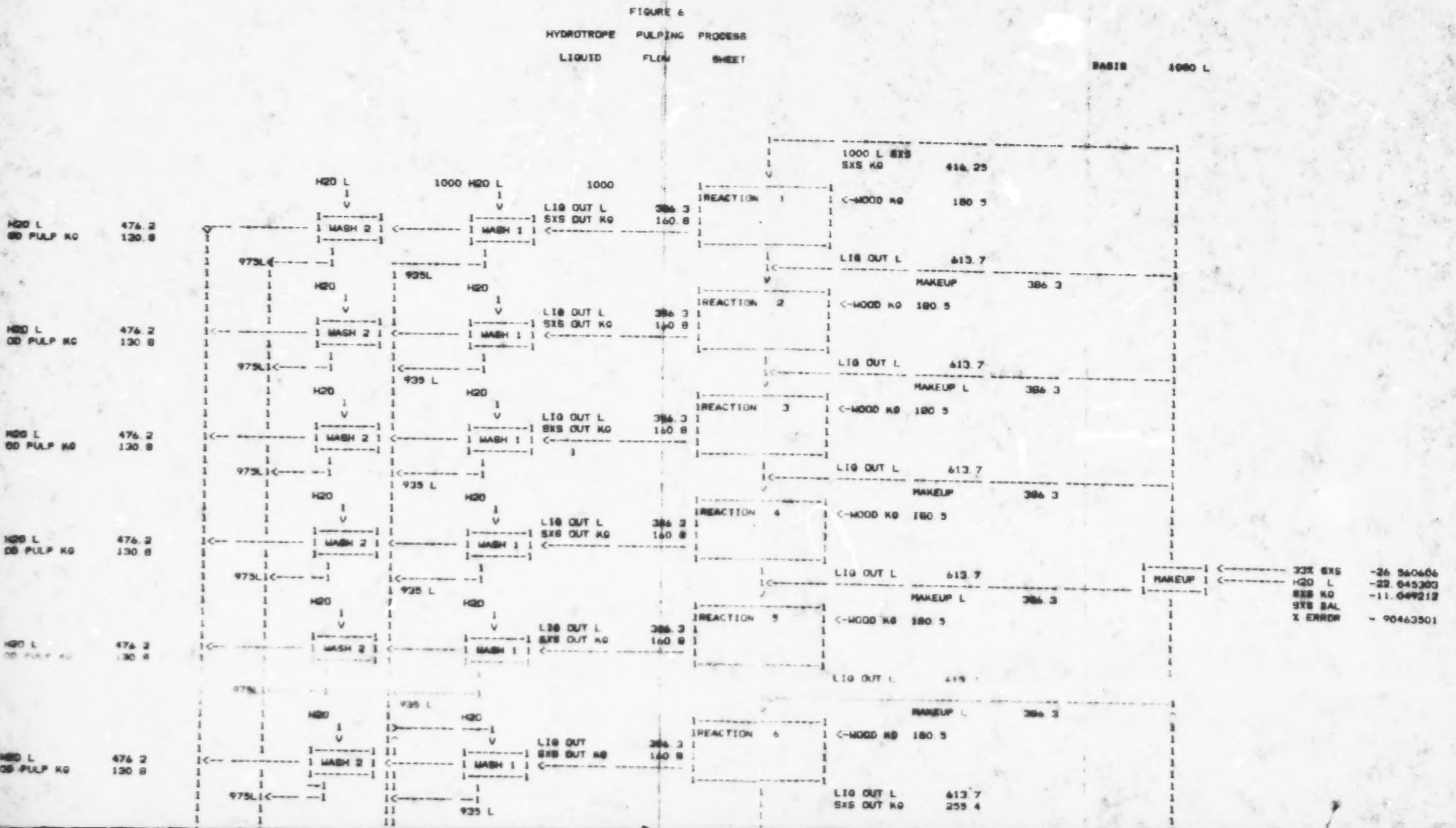
OTHER PRECAUTIONS

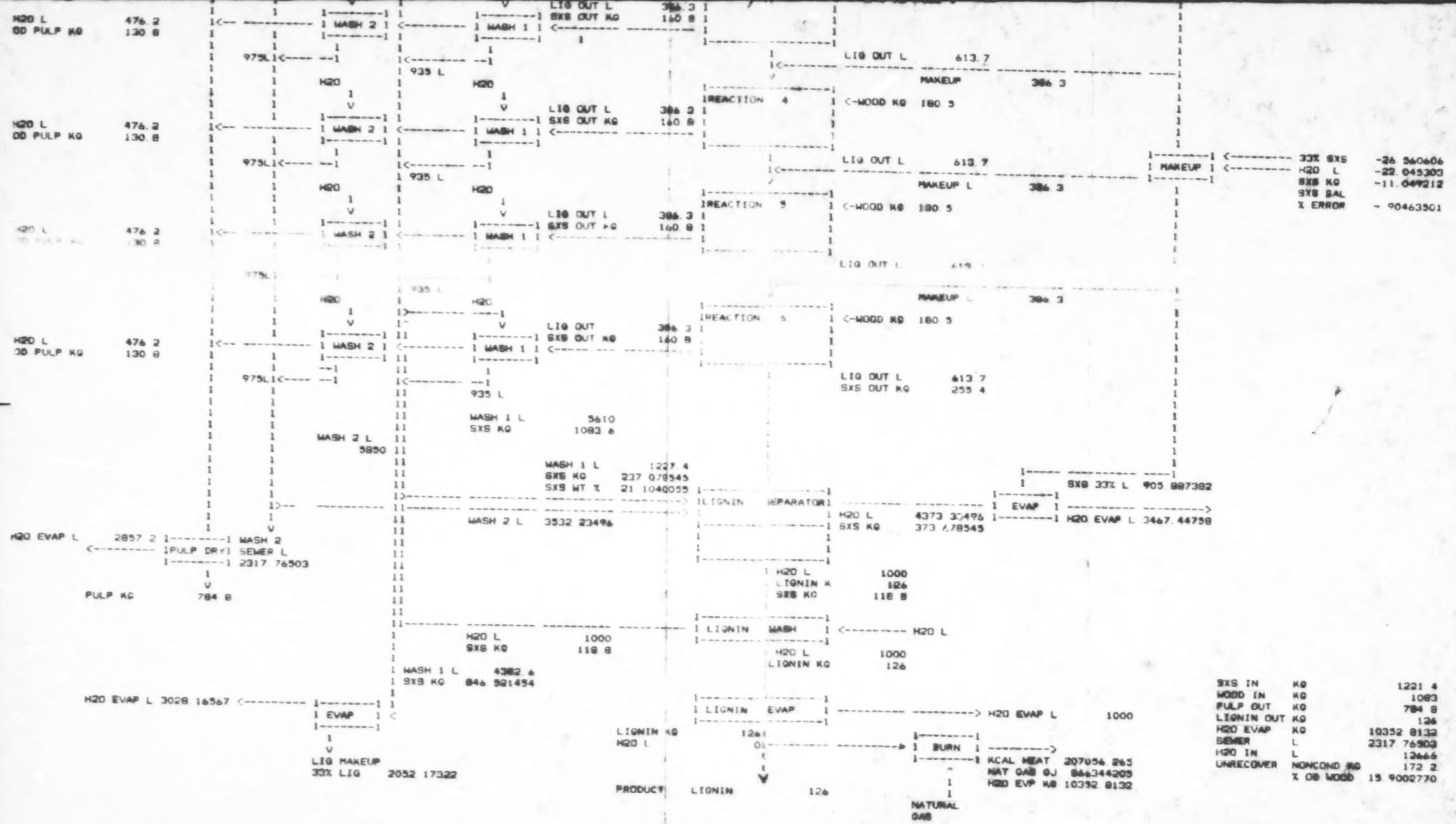
FIGURE 6

HYDROTROPE PULPING PROCESS SHEET

LIQUID FLOW

BASIS 1000 L




H20 L 476.2
OD PULP KG 130.8
WASH 2
975L
H20
WASH 1
935 L
LIQ OUT L 386.3
SXS OUT KG 160.8
REACTION 4
REACTION 5
<-WOOD KG 180.5
LIQ OUT L 613.7
MAKEUP 386.3
MAKEUP L
33% SXS -26.560606
H20 L -22.045303
SXS KG -11.049212
SXS BAL
% ERROR - 90463501
LIQ OUT
SXS OUT KG
WASH 1 L 5610
SXS KG 1083.6
WASH 2 L 5850
WASH 1 L 1227.4
SXS KG 237.078545
SXS WT % 21.1040055
WASH 2 L 3532.23496
SXS 33% L 905.887382
EVAP
H20 L 4373.30496
SXS KG 373.478545
H20 EVAP L 3467.44758
H20 EVAP L 2857.2
PULP DRY
SEWER L 2317.76503
PULP KG 784.8
H20 L 1000
LIGNIN K 126
SXS KG 118.8
LIGNIN WASH
LIGNIN KG 126
H20 EVAP L 3028.16567
EVAP
LIQ MAKEUP
33% LIQ 2052.17322
LIGNIN KG 126.1
H20 L 0
LIGNIN EVAP
H20 EVAP L 1000
PRODUCT LIGNIN 126
BURN
KCAL HEAT 207056.265
NAT GAS GJ 866344203
H20 EVP KG 10352.8132
NATURAL GAS
SXS IN KG 1221.4
WOOD IN KG 1083
PULP OUT KG 784.8
LIGNIN OUT KG 126
H20 EVAP KG 10352.8132
SEWER L 2317.76503
H20 IN L 12666
UNRECOVER NONCOND KG 172.2
% OD WOOD 15.9002770